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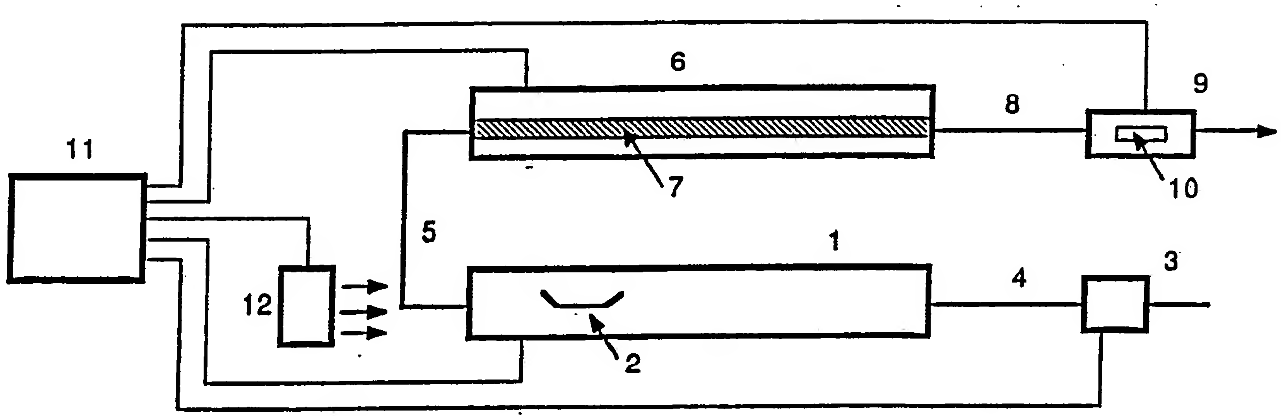


(57) Abstract

The invention comprises a method and an apparatus for determining (as Cetane Number) the ability of heavy fuels to self-ignite under diesel conditions. In a first stage, a known amount of oil sample is partially oxidized by exposure to an oxidizing gas while gradually increasing the temperature. In a second stage, a catalytic post-oxidation to CO2 and water is carried out and a detector monitors continuously the amount of CO2 produced as a function of temperature; the oil's Cetane Number is computed from the analytical data using a statistical model based on multivariate principal component analysis.

METHOD AND APPARATUS FOR DETERMINING THE ABILITY OF HEAVY FUELS TO SELF-IGNITE UNDER DIESEL CONDITIONS

The present invention comprises a method and an apparatus for determining (as Cetane Number) the ability of heavy fuels to self-ignite under diesel conditions by determining the Cetane Number. Diesel conditions imply that the fuel is injected as small droplets into compressed hot air.

While the Octane Number for a gasoline/air mixture indicates the gasoline's ability to be ignited in a controlled manner, a fuel's Cetane Number indicates its ability to be ignited under diesel conditions,

Cetane Number has not been defined for heavy fuels. Strictly it is therefore not correct to use this designation for the Ignition Number determined for such fuels, irrespective of the method employed. However, the Ignition Number determined for heavy fuels expresses the same property of heavy fuels as the Cetane Number does for distillates, since the scale for Ignition Number has been established by calibration with distillates of known Cetane Number. For the sake of simplicity, the term Cetane Number will be used also for heavy fuels in the description below.

Users of large marine engines have for a long time felt the need for a fast and reliable method for the determination of Cetane Number, since this gives a good indication of a fuel's autoignitibility. When fuels of varying quality are used, the knowledge of Cetane Number may be of primary importance, since the engine can be adjusted according to the properties of the fuel. It would be of great advantage for the Chief Engineer if the test method was so fast that the measurement might be carried out at the beginning of the bunkering procedure and the necessary apparatus so low priced that it might be kept aboard at all times. In this manner it would be possible for the Chief Engineer to determine the quality of the fuel at a sufficiently early stage for the bunkering to be interrupted if the fuel should appear to be of unacceptably low quality. The danger of a total engine breakdown would thus be almost completely eliminated.

Hitherto an estimation of ignition quality has not been possible, since the available methods are too time-consuming and require skilled laboratory personnel.

The standard method of determination of Cetane Number is an engine test where comparison with fuels of known Cetane Number is carried out in a special engine (CFR). Such a method is obviously not suitable for routine measurements, for example during bunkering.

Simpler and less costly tests have been used in laboratories recently. These methods involve heating up a fuel sample in a controlled atmosphere and measuring one or more parameters as a function of temperature.

For example, tests have been carried out in which the weight change was recorded while the sample was heated (thermogravimetry), but it has not been possible to give a satisfactory interpretation of the results. In addition the method requires expensive and delicate instrumentation and a skilled operator.

Attempts have also been made to combine thermogravimetry and differential thermal analysis or differential scanning calorimetry, where temperature changes and energy changes are measured, respectively. It was possible to interpret such measurements in terms of Ignition Number (Liddy et al.), however the apparatus is very costly and delicate and an expert is required to carry out and interpret the analysis.

Attempts have also been made to apply a modified DIN method for the characterization of heavy fuels. However, the equipment is not simple to use and has not been developed into a commercial product.

In another attempt simulation of a diesel cylinder by a combustion bomb has been used to determine the ignition quality of fuel oils. A model which probably will be suitable for laboratory use, will apparently be marketed. It is, however, expected that the equipment will be too large and complicated for use aboard ships and, to our present knowledge, no reliable correlation has been established between the ignition delay determined in the bomb and that in a real engine.

From the above it is apparent that all available methods for the determination of igniton properies of heavy fuels have

weaknesses which make them unsuitable for use aboard ships. The methods are both costly and complicated, in many cases involve the use of delicate equipment and in most cases require expert operators. No good correlation been demonstrated between the measured and observed data for some of the methods.

The present invention eliminates all the above mentioned shortcomings, since it offers a method which can be carried out aboard during bunkering and an apparatus which can be utilized by non-experts, the apparatus is neither costly nor demands any large space, so that it can be permanently installed aboard any ship. It is light and robust, it can be used under the influence of acceleration forces and it can be completely automatic. Above all, the method and the apparatus according to the invention, yield data which correlate very well with those measured directly in engines.

More precisely, the invention comprises a method for the determination of autoignitibility of heavy fuels under diesel conditions by the determination of Cetane Number, the procedure being the following. In a first stage, a known amount of an oil sample is partially oxidized in an oxidizing gas while gradually increasing the temperature. In a second stage, the partially oxidized oil components are oxidized catalytically to CO_2 and water while a detector continuously monitors the produced amount of CO_2 as a function of temperature, after which a computer algoritm based on statistical multivariate principal component analysis, yields the Cetane Number directly from the recorded amounts of CO_2.

The invention also comprises an apparatus in which the above procedure can be carried out, the characteristics of the apparatus being the following:

- a main reactor in which a small crucible for the oil sample can be placed, the reactor also including means for the introduction of the oxidizing gas and means for the emission of the oxidizing gas and oxidation products,
- a second reaction chamber which comprises a catalyst for the second stage oxidation of the products of partial oxidation to CO_2 and water and means for the emission of the reaction gases,

- a chamber including a detector for the detection of the CO2 content in the reaction gases,
- a processor unit which is able to generate the Cetane Number of the oil from the compiled CO2-values, using an algorithm based on multivariate principal component analysis, and also
- means for the heating of the oxidizing gas according to a preset temperature programme.

The oxidizing gas can be any gas which is able to bring about the desired oxidation of the oil. It is thus possible to utilize pure oxygen, air or any mixture of oxygen with gases which are inert with respect to the oil.

The temperature interval for oxidation and the rate of temperature increase of the oil sample are chosen in such a manner that the whole temperature region in which oxidation of the various components can take place is included, so that the generated data are reproducible and yield a good correlation with engine data. At the same time it is desirable that the analysis time be as short as possible.

Reproducible data are obtained when the oxidation is carried out in the temperature region 35 to 750 C in the first stage.

It has also been verified that heating rates of 20 to 50 C/min give very good results. These values are thus preferred for carrying out the analysis, and they imply an analysis time in the region of 15 - 35 minutes.

A good agreement between the Cetane Number determined by the analysis and that determined by engine test has been obtained using a heating rate as high as 40 C/min, which corresponds to an analysis time of ca 18 minutes. These parameters thus represent preferred conditions for the method according to the invention.

The second stage catalytic oxidation is not very critical with respect to the choice of temperature, but the latter must be sufficiently high to convert all oxidizable components to CO2 and water in this stage. From the practical point of view the necessary temperature depends - among other factors - on the type of catalyst used and on the geometry of

the second stage reactor. In laboratory experiments a platinum catalyst used at ca 1000 C was found to be satisfactory.

The choice of catalyst is not critical for the method according to the invention, so that any available commercial catalyst for the oxidation of hydrocarbons can be utilized. Catalysts with platinum as the active component were found to perform well. For the sake of economy and to obtain a high surface area/mass ratio for the catalyst, it is preferable that the active component is present in small quantities on the surface of a porous ceramic support.

It is also possible to add a cracking catalyst to the oil sample to be analysed, by which means it is possible to lower the final temperature from ca 750 to ca 620 C. At the same time the amount of residue which remains to be oxidized at the highest temperature, is smaller. Whether this represents a real time saving may depend on the ease of measuring the amount of the catalyst and the manner in which it is added.

The detector for the monitoring of CO2 may be an IR detector or another type of detector, for example one based on the the measurement of heat conductivity. Very good results have been obtained by the use of an IR detector and this is to be considered as the preferred type for the invention.

Fig. 1 shows a sketch drawing of the apparatus according to the invention.

Fig. 2 shows a correlation between Cetane Numbers determined by engine tests and by analysis for a number of oil samples. The experimental conditions are specified in the examples.

A more detailed description of the method and the apparatus is given below, with reference to figures.

Fig. 1 shows the main reactor (1), which contains a crucible (2) for the oil sample, the oxidizing gas is supplied by a pump (3) through a tubing (4). The oxidizing gas and the oxidation products pass from the main reactor (1) to the second reaction chamber (6) through a rigid tube (5). The oxidation products are completely converted to CO2 and water in the second reaction chamber (6) by means of a catalyst

(7). The gases then pass into a chamber (9) containing a detector (10) for quantitative determination of CO2. A processor unit (11) connected to the detector yields the Cetane Number directly from the recorded amounts of CO2. The processor unit can also be connected to the pump (3) to control the air flow, as well as the power to facilitate the temperature rise in the main reactor (1) and the temperature in the second reaction chamber (6).

The processor unit (11) can also control other process variables. It is, for example, an advantage to utilize a cooling fan (12) in conjunction with the main reactor (1), to be able to cool down the latter quickly between two subsequent analyses. The processor unit can control the start and stop of the cooling period.

Since the main reactor (1) is operated at at relatively low temperature during a certain part of the analysis period, and the second reactor (6) is always at a considerably higher temperature, a thermal barrier (not shown) is used between the two reactors.

The invention is illustrated below by an example which shows the correlation between Cetane Numbers detemined by analysis according to the invention, and Cetane Numbers determined by engine tests for the same oils.

Example:
21 different oil samples for which Ignition Numbers (Cetane Numbers) were determined by an engine test, were analysed by the method and apparatus according to the invention. The analysis parameters were kept constant and were the following:

oxidation gas: air:	100 ml/min
amount of oil	25 mg
initial temperature	35 C
final temperature	750 C
heating rate	40 C/min
time for analysis	18 min

A statistical model based on multivariate principal component analysis has been developed from the analytical data. The

model was then optimized to yield an unambiguous correlation between the Cetane Numbers from engine tests and analyses, respectively. The correlation is shown in Fig. 2.

CLAIMS

1. A method for the determination of the autoignitibility of heavy fuels under diesel conditions by determining the Cetane Number, c h a r a c t e r i z e d i n t h a t in a first stage, a known amount of an oil sample is partially oxidized in an oxidizing gas while gradually increasing the temperature; in a second stage, the partially oxidized oil components are oxidized catalytically to $CO2$ and water while a detector continuously monitors the produced amount of $CO2$ as a function of temperature, after which a computer algorithm based on statistical multivariate principal component analysis, yields the Cetane Number directly from the recorded amounts of $CO2$.

2. A method as claimed in claim 1, c h a r a c t e r i z e d i n t h a t in said first stage an initial temperature of 35 oC and a final temperature of 750 oC is employed.

3. A method as claimed in claim 1 or 2, c h a r a c t e r i z e d i n t h a t the temperature of said oxidizing gas in said first stage is increased at a rate of 20 - 50 oC/min during a period of 15 - 35 minutes.

4. A method as claimed in claim 1 or 2, c h a r a c t e r i z e d i n t h a t the temperature of said oxidizing gas in said first stage is increased at a rate of 40 oC/min during a period of about 18 minutes.

5. A method as claimed in claim 1, c h a r a c t e r i z e d i n t h a t said second stage catalytical oxidation is performed at 1000 oC.

6. A method as claimed in claim 1, c h a r a c t e r i z e d i n t h a t said catalyst used for the second stage oxidation is an oxidation catalyst, preferably containing platinum either alone, or as an active component on the surface of a ceramic support.

7. A method as claimed in claim 1, c h a r a c t e r i z e d i n t h a t said detector used for monitoring the $CO2$-content is an IR-detector.

8. Apparatus for the performance of the method as claimed in claim 1, c h a r a c t e r i z e d by the following:
   a) a main reactor (1) in which a small container (2) for the oil sample can be placed, means (3,4) for the introduction of the oxidizing gas and means (5) for the emission of the oxidizing gas and oxidation products,
   b) a second reaction chamber (6) which comprises a catalyst (7) for a second stage oxidation of the products of partial oxidation to CO2 and water, and means (8) for the emission of the reaction gases,
   c) a chamber (9) including a detector (10) for the monitoring of the CO2 content in the reaction gases,
   d) a processor unit (11) programmed to generate the Cetane Number of the oil from the recorded CO2-values, using an algorithm based on mulitvariate principal component analysis, and also
   e) means for the heating of the oxidizing gas according to a preset temperature programme.

9. Apparatus as claimed in claim 8, c h a r a c t e r i z e d i n t h a t said detector for the monitoring of the CO2-content is an IR-detector.

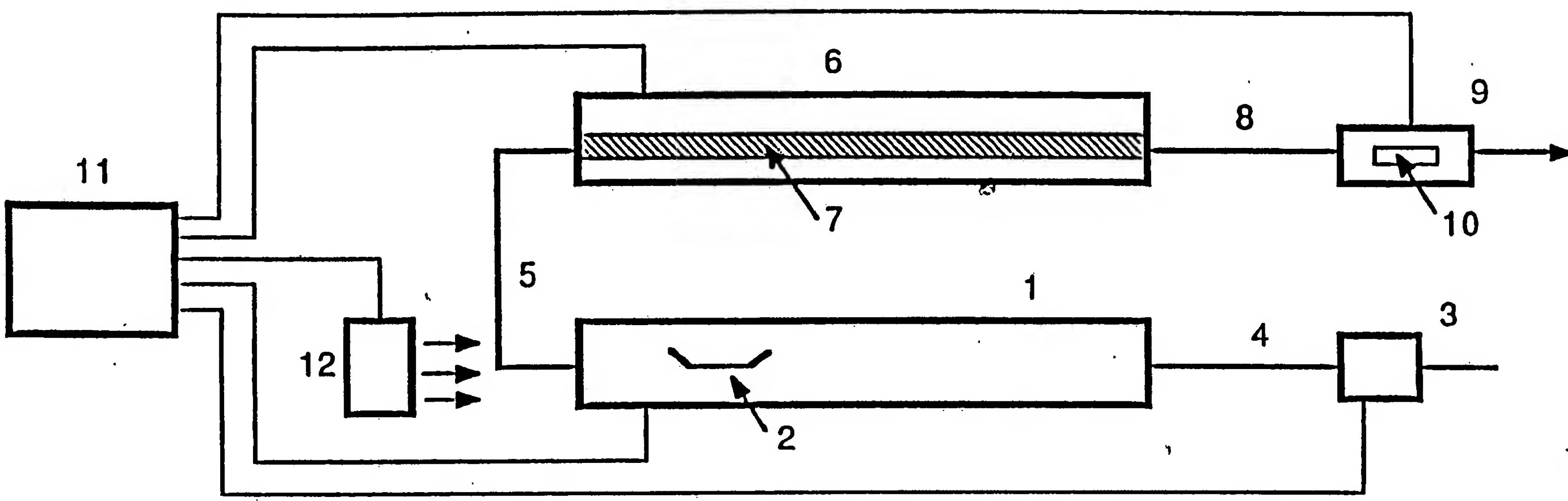
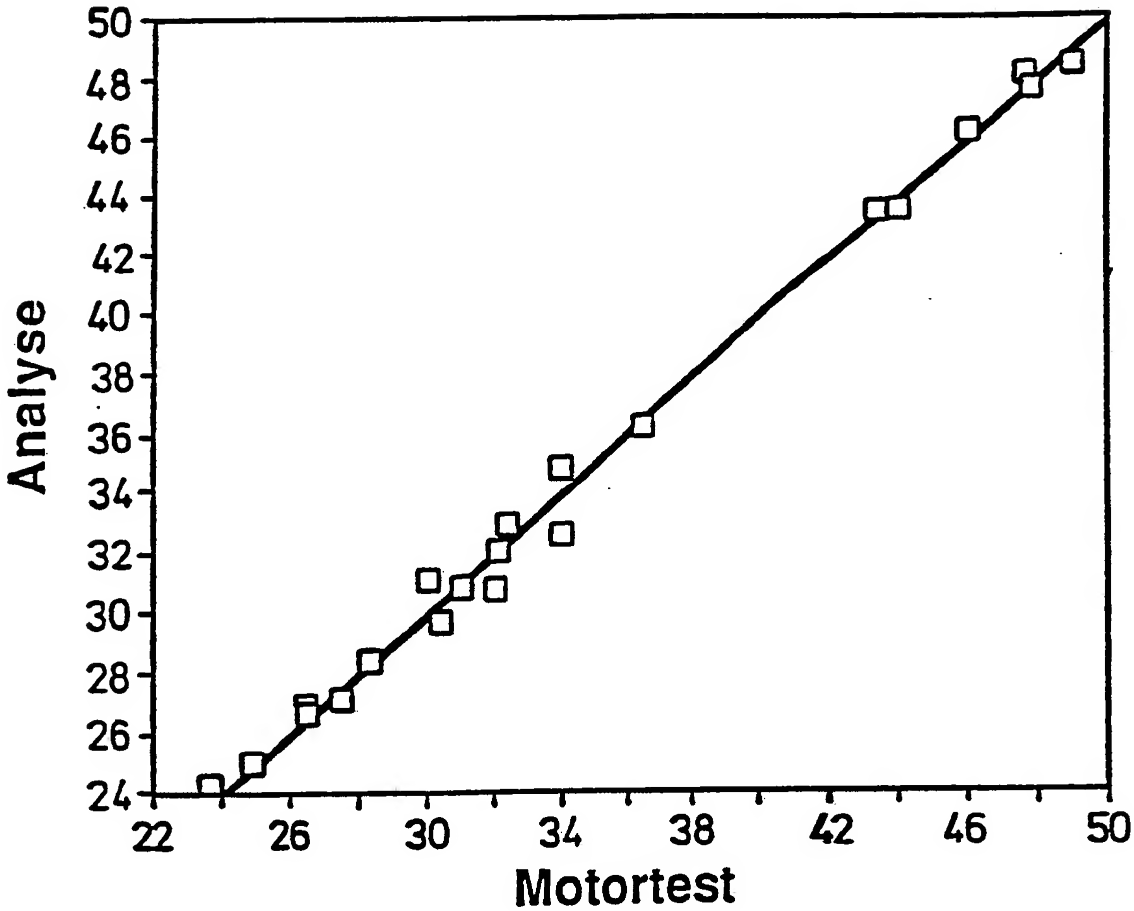


Fig. 1


Analyse
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Motortest

Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No PCT/NO89/00017

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC 4

G 01 N 33/22

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC 4	G 01 N
US Cl	23; 436

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 4 057 393 (PAUL A. BUDZAK ET AL) 8 November 1977 whole document	1-9
A	US, A, 3 738 808 (GLENN P. CUNNINGHAM ET AL) 12 June 1973 whole document	1-9
A	DE, C2, 2 524 703 (GULF RESEARCH & DEVELOPMENT CO.) 4 March 1976 whole document	1-9
A	EP, A2, 0 143 571 (MOBIL OIL CORPORATION) 5 June 1985 whole document	1-9

* Special categories of cited documents: [10]
"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
1989-05-29	1989 -05- 31
International Searching Authority	**Signature of Authorized Officer**
Swedish Patent Office	Inger Löfgren